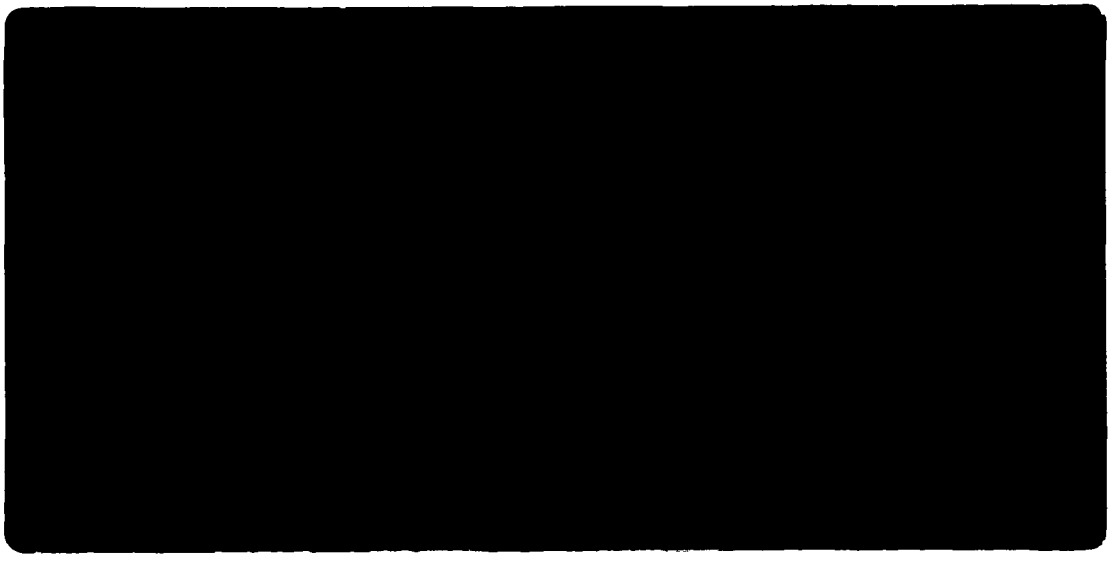
Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES



NUMBER 412

DEGRADATION OF DIBENZODIOXIN DURING CHLORINE DIOXIDE BLEACHING OF KRAFT PULP

A. DAUBE, M.R. KARIM, D.R. DIMMEL,
T.J. MCDONOUGH, AND S. BANERJEE

JANUARY 1992

Degradation of Dibenzodioxin During Chlorine Dioxide Bleaching of Kraft Pulp

A. Daube, M.R. Karim, D.R. Dimmel, T.J. McDonough, and S. Banerjee

Submitted to
Environ. Sci. Technol.

Degradation of Dibenzodioxin During Chlorine Dioxide Bleaching of Kraft Pulp

Alison Daube, Mohammed R. Karim, Donald R. Dimmel,
Thomas J. McDonough, Sujit Banerjee

Institute of Paper Science and Technology
575 14th St. NW
Atlanta GA 30318

Abstract

The degree of sorption of dibenzodioxin (DBD) to pulp varies with the lignin content of the latter. DBD is rapidly degraded by chlorine dioxide in aqueous solution but is much more stable in the presence of semi-bleached pulp, suggesting that sorbed DBD is far less reactive than the freely dissolved material. Degradation products include the 2-chloro derivative (5%) and products inextricably bound to pulp (28%).

Introduction

Chlorinated organic compounds are formed during bleaching with chlorine and chlorine dioxide. The component that has been of greatest interest is 2,3,7,8-tetrachlorodibenzodioxin (TCDD). One of the principal sources of TCDD is dibenzodioxin (DBD) which may originate in the defoamer used in processing the pulp (1). The reactivity and pulp:water distribution of DBD and its derivatives under typical bleaching conditions are, therefore, essential to the understanding of TCDD formation. Furthermore, as a stable hydrophobic material, DBD serves as a model for other substrates that may undergo chlorination. We have studied the reactivity and distribution of DBD in pulp/water systems during chlorine dioxide bleaching, and in this paper we provide a broad overview of its fate.

Materials and Methods

A loblolly pine Kraft pulp of kappa number 40.6 (≈6% lignin) and a bleached hardwood pulp of kappa number <1 (no measurable

lignin) were used. The pulps were disintegrated, reformed into mats by filtration through coarse sintered glass and air-dried. ClO_2 was determined iodometrically. Tritiated water was purchased from New England Nuclear, DBD from MSD Isotopes, and 1- and 2-chlorodibenzodioxin from Ultra Scientific.

Synthesis of tritiated DBD

Synthetic trials for the preparation of tritiated DBD were first conducted with ^2H_2O. Since DBD is thermally stable, electrophilic deuteration was attempted at the high temperature (195°C) and dilute acid (4% HCl in D_2O) conditions (2) used to label simple aromatics. However, <2% isotope incorporation occurred after 43 hours indicating that DBD is too deactivated to be labeled by electrophilic exchange. Nevertheless, the low reactivity establishes that once prepared by other means, [^{3}H]DBD should be very resistant to isotope loss.

[^{3}H]DBD was prepared by condensing [^{3}H]catechol with o-chloronitrobenzene (Scheme 1). The labeled catechol was prepared by refluxing catechol in 5% HCl containing 1μCi of ^3H_2O for 24 hours. A trial run in deuterated media showed that complete exchange occurs under these conditions. Following reflux, the solution was diluted with ethanol and then distilled to near-dryness. The ethanol addition-distillation sequence was repeated twice to maximize azeotropic removal of tritiated water and to reduce carryover of tritium to the next step.

The labeled catechol was refluxed under nitrogen with excess o-chloronitrobenzene (to promote consumption of the labeled cate-

chol) for 1 hour in alkaline DMF. The products were extracted into methylene chloride and the labeled DBD was separated by preparative thin layer chromatography on silica with 5% methanol in methylene chloride as the eluent. The other labeled components, [^{3}H]catechol and [^{3}H]H_2O, are strongly retained under these conditions. The [^{3}H]DBD was isolated from the TLC plate with methylene chloride. Its identity and purity was verified by electron impact GC-MS. A specific activity of 1.8 μCi/mmole was calculated from liquid scintillation counting and reversed-phase hplc.

Recovery Studies

DBD was quantitatively recovered from water-pulp mixtures with methylene chloride extraction at room temperature. However, if the mixture is heated (60°C, 30 min.) under typical bleaching conditions, only 40-60% of DBD was recovered by methylene chloride extraction of the pulp mixture. Clearly, a significant fraction of the DBD volatilized. However, enough material remained in solution to react with the bleaching agent.

Sorption Studies

Oven-dried pulp (0.3 g) was added to 30 mL of water. ^{3}H-DBD (2,000 dpm) was added and the mixture was stirred vigorously and allowed to equilibrate overnight. When the substrate was a 40 kappa pulp, the water and pulp was separated using a table-top centrifuge. When the substrate was a fully bleached pulp, the centrifugal separation was incomplete and filtration through medium porosity glass was necessary.

The separated pulp was extracted with methylene chloride, and both the extracts and the aqueous phase were counted. For the 40 kappa pulp, the pulp:water ratio of the counts was 2.1. A second experiment with unbleached DBD and the reactants at ten times the previous levels gave a 2.2 ratio. The analysis in this case was by hplc (diode array detection). For the fully bleached pulp, 0.3 g. of pulp was equilibrated with 50 mL of a DBD solution for 16 hours. Extraction and hplc analysis as described above yielded a pulp:water ratio of 0.27.

Bleaching Experiments

An aqueous solution of DBD was prepared by adding 1 mL of a methanolic concentrate of DBD to water (100 mL) in a 500 mL round-bottom flask. The 40 kappa pulp (3 g) was then added and the mixture was mechanically stirred and brought to $60\pm5^{o}C$. A freshly standardized solution of ClO_2 (nominally containing 1-5% of Cl_2) was introduced under the surface of the liquid. The kappa factor (not including molecular chlorine) was 0.25. The mixture was then stirred vigorously for 30 min, quenched with 0.1N sodium thiosulfate, cooled to room temperature and extracted with methylene chloride. A longer contact period was used for the time-course experiments.

The concentrated extracts were analyzed by GC-MS as well as by hplc. The principal product, 2-chlorodibenzodioxin, was identified by mass spectral and hplc comparison with authentic materials. Although the electron impact mass spectra and the gc retention of 1- and 2-chlorodibenzodioxins are similar, the two

isomers are easily resolved by hplc on a reversed phase column. The chlorodibenzodioxin yield was small (5%), and the absence of other detectable methylene chloride extractables suggests that the remaining products were polar.

Results and Discussion

Owing to its high Henry's Law Constant of 12.29 atm. m^3 mol^{-1} (3) DBD can potentially volatilize from water, although its rate of removal may be retarded by association to pulp. Our recovery studies show that about half the material volatilizes at 60°C in 30 minutes under our conditions. Volatilization should be less important in a bleach plant where the surface area:volume ratio is much lower.

The DBD pulp:water distribution coefficient for the 40 kappa pulp is about 200. This value can be interpreted with reference to sediment-water systems where sorption occurs principally to the organic carbon fraction of sediment. Karickhoff has shown (4) that sediment:water distribution coefficients normalized with respect to sediment organic carbon content, K_{OC}, can be related to the octanol:water partition coefficient (K_{OW}) of the solute through eq (1)

$$\log K_{OC} = \log K_{OW} - 0.21 \qquad (1)$$

If pulp behaves similarly to sediment, then eq (1) used with a DBD log K_{OW} of 4.37 (5) and a 45% estimate for the organic carbon content of pulp predicts a distribution coefficient of about 7,000.

This value falls sharply if it is assumed that sorption occurs primarily to the lignin fraction of pulp. Garbarini and Lion (6) studied the sorption of toluene and trichloroethylene to lignin and cellulose particles, and obtained distribution coefficients of 120-150 for lignin:water and only 0-2 for cellulose: water partitioning. The organic carbon contribution from the lignin in our pulp is only about 4% since lignin is approximately 62% carbon (7). If sorption to cellulose is neglected, then equation (1) predicts a K_{OC} value of about 600. While this estimate is threefold higher than the measured value, it is reasonable given that the particle size of our pulp fibers was much larger than that of the sediments used to develop eq 1.

The finding that sorption to bleached pulp is about eightfold lower than that to kappa 40 pulp emphasizes the importance of lignin as the primary sorbent. However, the degree of sorption to the bleached pulp is still appreciable and suggests that DBD can bind to non-lignin components. Extractives that remain in bleached pulp are possible candidates, although at 0.1-0.2%, they cannot account for the full extent of the observed sorption. Also, pulp retains a considerable amount of water and it is very difficult to completely separate the two phases under equilibrium conditions. Hence, K_{OC} will be biased high from solution carryover.

Garbarini and Lion (6) used extracted lignin whereas our results are based on residual lignin incorporated in the pulp matrix. The K_{OC} value from the 40 kappa pulp is broadly consist-

ent with Karickhoff's equation and suggests that lignin in pulp behaves similarly to the chemically extracted material. This opens the possibility of estimating sorption to pulp only from a knowledge of solute K_{ow} and the properties of the pulp.

Addition of a ClO_2/Cl_2 solution to an aqueous solution of DBD degrades the substrate as shown in Figure 1. DBD loss in the control experiment reflects volatilization. The chlorination half-life of approximately 30 minutes is of the same magnitude as the residence time of pulp in a commercial bleaching stage, indicating that dissolved DBD would be substantially degraded. Results from corresponding experiments conducted in the presence of the kappa 40 pulp are illustrated in Figure 2. Clearly, DBD reactivity is strongly inhibited through sorption, presumably to lignin. Possibly, the compound is protected by lignin by virtue of its reduced access to the bleaching agent. It seems that DBD degradation will be optimum when the lignin is substantially depleted and the DBD is released to the aqueous phase.

Product distribution was measured from bleaching experiments with [^{3}H]DBD. The kappa 40 pulp and water were separated after quenching, extracted with methylene chloride and analyzed by both hplc for DBD and liquid scintillation counting for total activity. Of the original activity, 16% was found in the pulp extracts and 16% in the aqueous phase. By hplc, 8% of the initial DBD appeared in the water and 4% was found in the pulp extract. The pulp:water DBD ratio is biased towards water in contrast to our sorption experiments with the kappa 40 pulp. This follows from

the removal of lignin during bleaching which would reduce the sorptive capacity of the pulp. Twenty eight percent remained in the pulp as inextricable material as determined by direct counting of the pulp fibers. Essentially all of the activity applied could be accounted for after allowance for volatilization.

Methylene chloride extracts of the pulp and the spent bleaching liquors contained a small amount (5 mole percent) of 2-chlorodibenzodioxin. The efficiency of conversion of this material to the 2,3,7,8-tetrachloro-derivative is unknown.

Conclusions

Sorption of DBD to pulp occurs principally to the lignin fraction. In laboratory scale chlorine dioxide bleaching experiments 5% was converted to 2-chlorodioxin, and 28% to products inextricable from pulp. The remainder was unreacted DBD and unidentified material. Sorption to (the lignin component of) pulp greatly reduced the reactivity of DBD.

Literature Cited

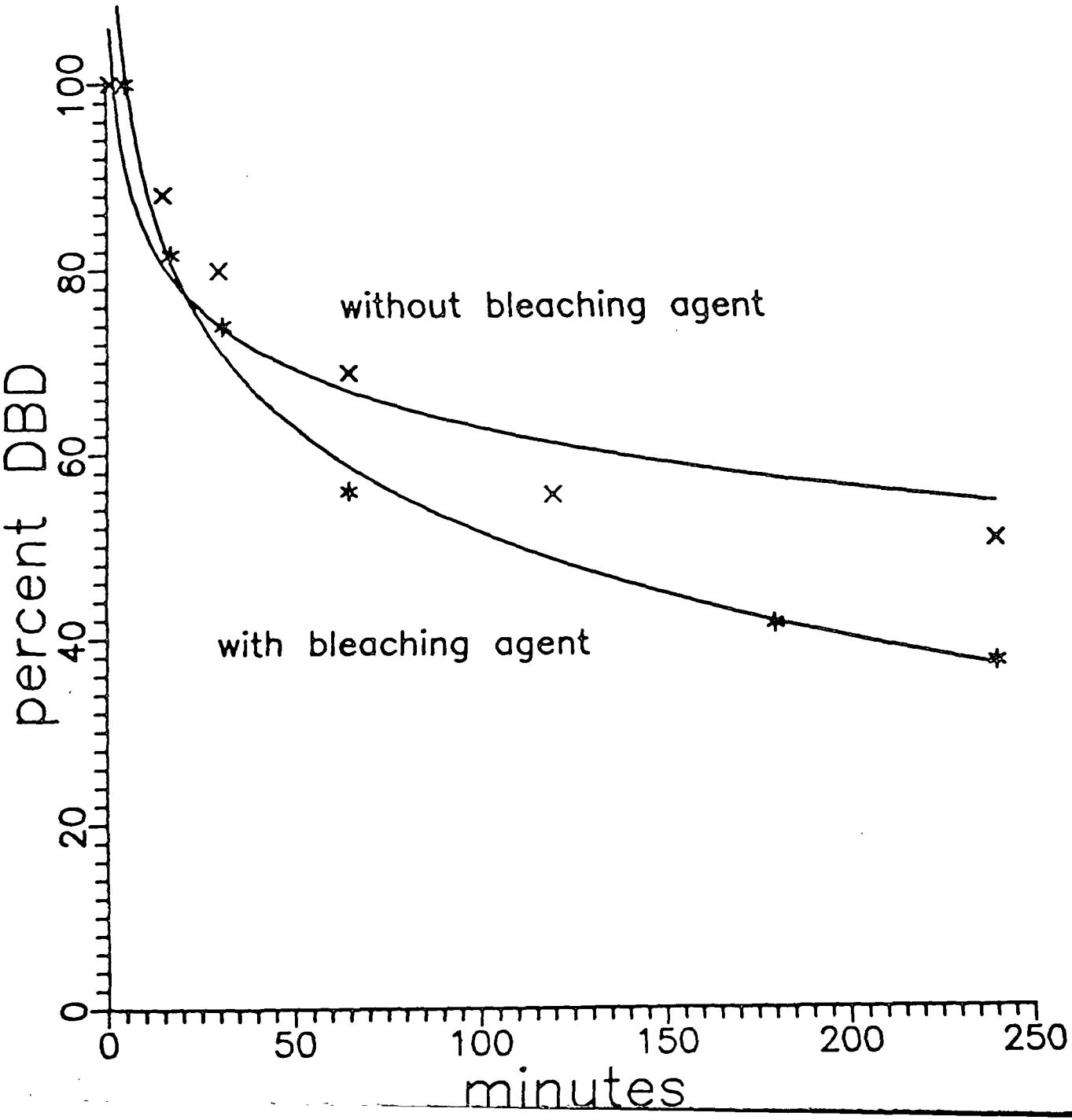
1. Voss, R.H.; Luthe, C.E.; Fleming, B.I.; Berry, R.M.; Allen, L.H. Pulp Paper Can. 1988, 12, T401.
2. Werstiuk, N.H.; Kadai, T. 1973, Can. J. Chem., 51, 1485-1486.
3. Shiu, W.Y.; Doucette, W.; Gobas, F.A.P.C.; Andren, A.; Mackay, D. Environ. Sci. Technol., 1988, 22, 651-658.
4. Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Water Research 1979, 13, 241-248.
5. Doucette, W.J.; Andren, A.W. Environ. Sci. Technol. 1987, 21, 821-824.
6. Garbarini, D.R.; Lion, L.W. Environ. Sci. Technol. 1986, 20, 1269-1273.
7. Lai, Y.Z.; Sarkanen, K.V. in "Lignins: Occurrence, Formation, Structure and Reactions"; Sarkanen, K.V., Ludwig, C.H. Eds., Wiley-Interscience, 1971.

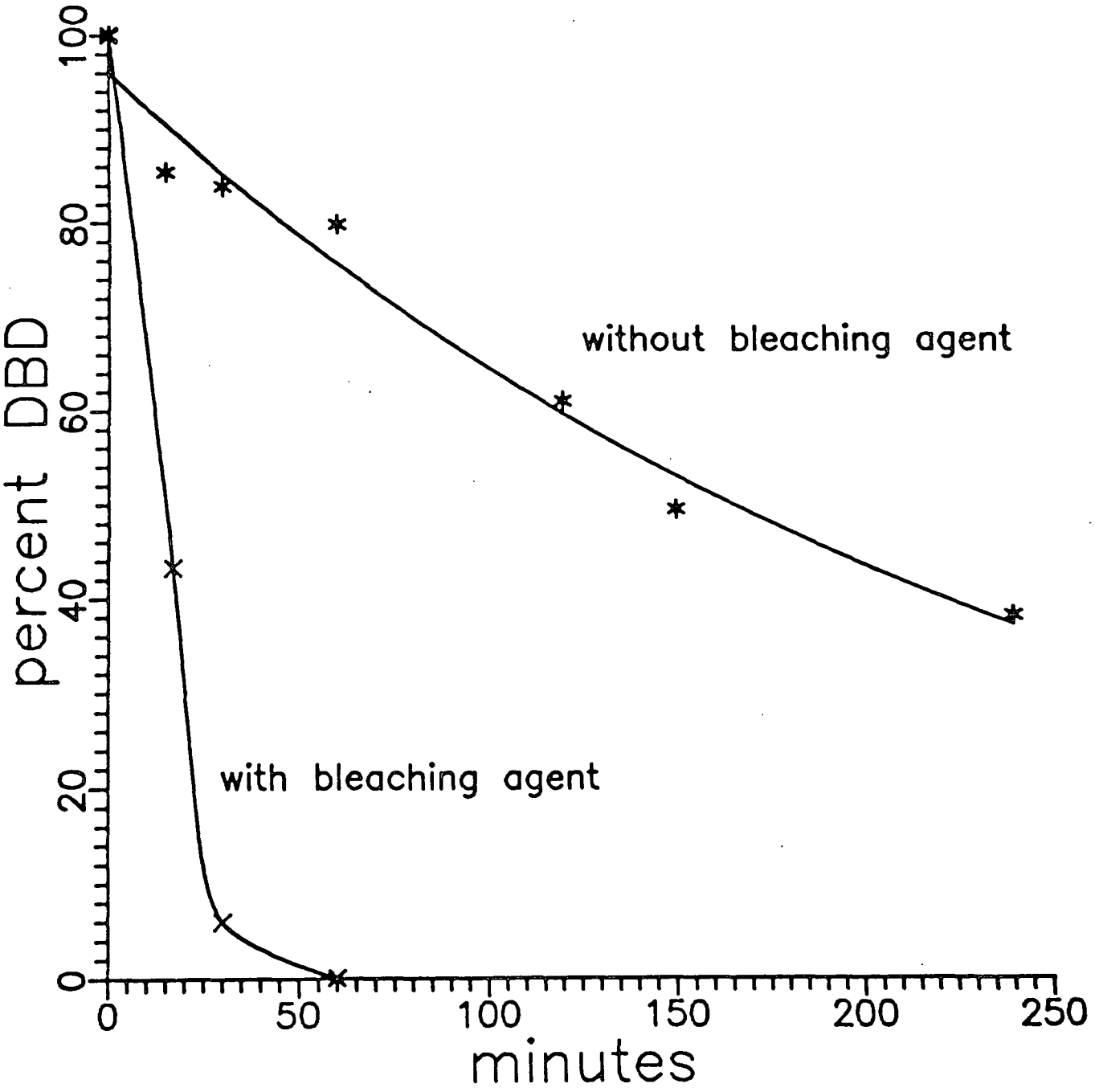
Captions to Figures

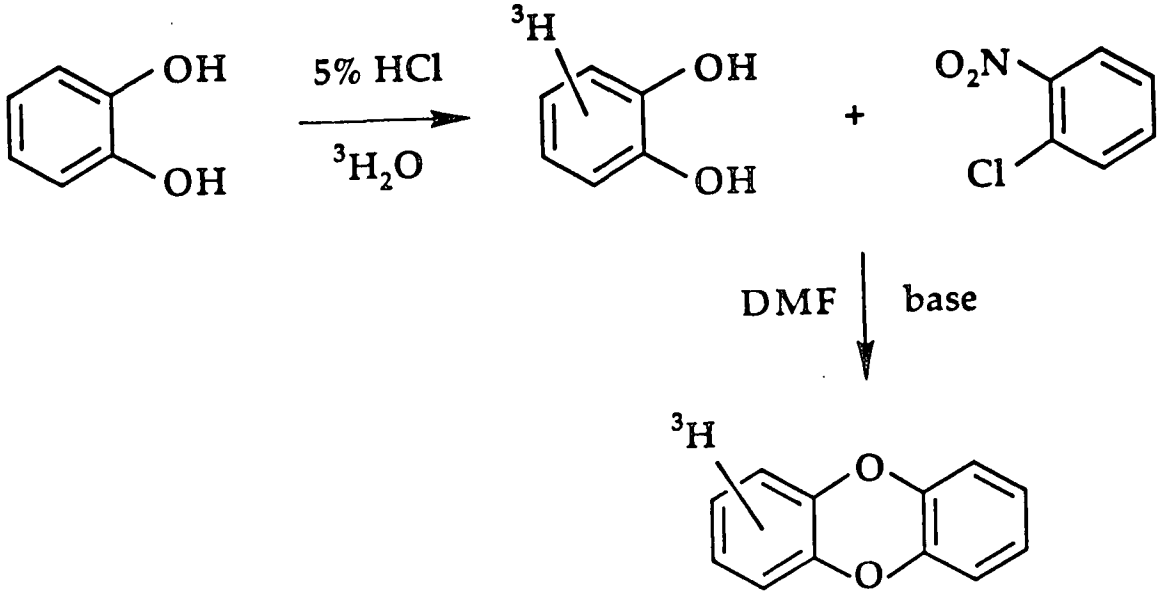
Figure 1 Loss of DBD from water

Figure 2 Loss of DBD from pulp-water suspensions

FIG 1


percent DBD
0
20
40
60
80
100
0
50
100
150
200
250
minutes
without bleaching agent
with bleaching agent


percent DBD
0
20
40
60
80
100
0
50
100
150
200
250
minutes
without bleaching agent
with bleaching agent



Scheme 1